

VARIATIONS OF THIOACETAMIDE TREATMENTS ON CIGS SOLAR CELLS ON STAINLESS STEEL SUBSTRATES – CORRELATIONS TO DEVICE PERFORMANCE

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ABSTRACT

The details of design of experiment (DOE) studies involving thioacetamide treatment performed on $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ (CIGS) deposited on stainless steel are discussed. CIGS films were treated in an aqueous InCl_3 /thioacetamide (CH_3CSNH_3) bath varying time, temperature and salt as well as CH_3CSNH_3 concentration in order to determine the optimum conditions for surface sulfurization. Subsequent device completion employing a CBD CdS buffer was performed under nominally identical conditions. The resulting devices were compared on the basis of deposition conditions including untreated control specimens. Device efficiencies in this study ranged from 6 to 11% and did not show significant improvement over untreated controls. Procedures, results, and possible causes for disagreement with earlier studies are discussed.

INTRODUCTION

An additional chemical treatment of the CIGS absorber with thioacetamide-containing solutions has recently been reported to yield up to 20% relative device performance improvements [1],[2]. Short immersion of the as-deposited CIGS layers into solutions containing thioacetamide (CH_3CSNH_3) along with a group III metal salt, such as InCl_3 , are believed to lead to the formation of a thin sulfide layer and/or surface passivation via S incorporation into the CIGS. This modification, prior to CdS deposition, is intended to improve performance at the junction by reducing the conduction band offset or reducing the number of recombination centers.

The applicability of such a surface treatment on CIGS devices prepared on steel foils at Global Solar Energy was examined. Design of experiment matrices exploring the variables of time, temperature, salt and CH_3CSNH_3 solution concentrations were utilized. Subsequent device completion and I-V testing at ITN followed standard procedures. Optimum InCl_3 and CH_3CSNH_3 concentrations were determined and found to be consistent with those quoted in the literature.

EXPERIMENT

CIGS deposition by co-evaporation onto stainless steel substrates in a production roll-to-roll process was performed at Global Solar Energy. Further details of this process are reported elsewhere [3]. CIGS from a $48' \times 12'$ web section was cut into $3'' \times 3''$ coupons and the compositional uniformity of the samples was verified by x-ray fluorescence (XRF) to be spatially uniform within $\pm 5\%$ (relative) for the atomic ratios $\text{Cu}/(\text{In}+\text{Ga})$ and $\text{Ga}/(\text{In}+\text{Ga})$.

For the thioacetamide treatment, de-ionized (DI) water and InCl_3 were combined in a heated beaker, allowed to equilibrate at 60°C prior to adding thioacetamide stock solution and the CIGS coupon. The respective purities of the thioacetamide and InCl_3 salt were 99% and 99.99%. Stock solutions of thioacetamide and InCl_3 salt were made with concentrations of 0.4M and 0.06M, respectively.

The basic procedure described above was performed in two formats. The differences between these formats involve timing of coupon and water introduction, as well as beaker type. In the first experimental set, total solution amounts are calculated to fill 400 ml of a 600 ml single-walled beaker on a hot plate. All water other than that contained in the thioacetamide stock solution is added with the InCl_3 . The coupon is introduced only after the 400 ml solution reaches 60°C . Convection is ceased and coupons are immersed for the prescribed amount of time.

In a variation of the procedure, total solution amounts are calculated to fill 725 ml of a 1000 ml jacketed beaker. Only enough water is added with the InCl_3 to bring the volume to 500 ml. The coupon is introduced into the InCl_3 solution and allowed to heat to temperature before thioacetamide addition (volume adjusted with DI water to 225 ml). This point is used as the reference for immersion time and the solution is stirred constantly.

In order to expedite the process of optimizing the thioacetamide treatment a Design of Experiment approach was employed to minimize the number of trials necessary to define the

effects within the variable space. The four variables under consideration for optimizing a thioacetamide treatment for a specific salt were: (1) salt concentration, (2) thioacetamide concentration, (3) bath temperature, and (4) treatment time. The optimized bath temperature was determined in a separate study to be 60°C, allowing the number of variables to be reduced to three. Levels for each of the remaining variables were set to a low, medium and high value – i.e., the thioacetamide concentrations were 0.0M, 0.05M and 0.1M, the InCl_3 concentrations were 0.0M, 0.0125M and 0.025M, and immersion times were 1, 6 and 11 seconds. These values were chosen to overlap with values used in previous studies [1],[2]. The ensuing 9 conditions of the $3^{(k-p)}$ matrix were completed in random order to remove the effect of potential process variability. In addition to the treated samples an untreated control piece was fabricated for each batch of devices.

Following thioacetamide treatment, devices were completed using standard CBD CdS within 1 hour of the thioacetamide step. Sputtered resistive ZnO, conductive ITO and e-beam evaporated Ni-Al grids were simultaneously deposited on all samples. Devices of 1.16 cm² total area were mechanically isolated, and AM1.5 current-voltage data was generated. No anti-reflective coating was applied.

RESULTS AND DISCUSSION

Experiments in the DOE matrix were performed according to the two treatment procedures described above. Treatment conditions and average device results are summarized in Table 1, Table 2(a) and Table 2(b). The results in Table 2(b) are based on a repeat of the series listed in Table 2(a), thus investigating process repeatability. In each case, the coupon labeled “0” represents the control specimen, finished without thioacetamide treatment. Average device parameters were computed after removal of statistically invalid outliers (shunted devices).

Table 1. Conditions and device results for treatment as per the single-walled beaker procedure described earlier.

Sample #	Salt Conc. (M)	Thio Conc. (M)	Time (s)	Avg η [%]	Avg V_{oc} [V]	Avg. J_{sc} [mA/cm ²]	Avg FF [%]
B0				8.23	0.601	23.82	0.58
B1	0.000	0.00	1	5.83	0.490	23.20	0.51
B2	0.000	0.10	6	6.63	0.529	23.31	0.53
B3	0.000	0.05	11	7.55	0.607	23.15	0.54
B4	0.025	0.10	1	8.49	0.608	24.40	0.57
B5	0.025	0.05	6	8.23	0.605	23.82	0.57
B6	0.025	0.00	11	8.08	0.605	23.25	0.58
B7	0.005	0.05	1	5.54	0.511	22.23	0.48
B8	0.005	0.00	6	6.95	0.598	23.39	0.50
B9	0.005	0.10	11	7.73	0.608	23.35	0.55

Table 2. Conditions and device results for treatments performed as per the jacketed beaker procedure described earlier.

a)

Sample #	Salt Conc. (M)	Thio Conc. (M)	Time (s)	Avg η [%]	Avg V_{oc} [V]	Avg. J_{sc} [mA/cm ²]	Avg FF [%]
C0				10.21	0.603	25.27	0.67
C1	0.0000	0.00	1	9.98	0.607	24.92	0.66
C2	0.0125	0.10	1	9.23	0.594	23.10	0.67
C3	0.0250	0.05	1	9.33	0.578	24.49	0.66
C4	0.0000	0.10	6	8.90	0.576	23.33	0.66
C5	0.0125	0.05	6	10.44	0.600	25.11	0.69
C6	0.0250	0.00	6	8.90	0.581	22.59	0.68
C7	0.0000	0.05	11	10.34	0.590	25.61	0.68
C8	0.0125	0.00	11	10.74	0.613	25.94	0.68
C9	0.0250	0.10	11	8.89	0.572	23.31	0.67

b)

Sample #	Salt Conc. (M)	Thio Conc. (M)	Time (s)	Avg. η [%]	Avg. V_{oc} [V]	Avg. J_{sc} [mA/cm ²]	Avg. FF [%]
D0				7.91	0.57	21.67	0.64
D1	0.0000	0.00	1	9.09	0.586	23.72	0.65
D2	0.0125	0.10	1	8.71	0.578	23.32	0.65
D3	0.0250	0.05	1	8.31	0.58	23.36	0.62
D4	0.0000	0.10	6	9.18	0.590	23.38	0.67
D5	0.0125	0.05	6	9.77	0.593	24.71	0.67
D6	0.0250	0.00	6	8.66	0.59	21.73	0.67
D7	0.0000	0.05	11	8.82	0.59	22.74	0.66
D8	0.0125	0.00	11	9.00	0.59	23.73	0.65
D9	0.0250	0.10	11	8.56	0.58	23.14	0.64

For each of the 3 matrices, a pair-wise comparison of treated and control coupons did not indicate a significant improvement as a result of thioacetamide/ InCl_3 immersion condition with respect to the controls. The lack of a 20% relative improvement in device performance, as has been reported elsewhere [1],[2], implies that the benefit of this technique may be dependent on the CIGS chemistry or subsequent buffer/window layer deposition rather than the thioacetamide treatment conditions.

Analysis of device data from the treated samples via the ANOVA approach for the single-walled beaker set in Figure 1(a) reveals a significant linear correlation with InCl_3 concentration while the dependence on CH_3CSNH_3 concentration is not statistically significant. In contrast, experiments carried out on CIGS from the same section of web, but in the jacketed beaker, Figure 1(b), suggest an optimum combination of thioacetamide and salt concentrations, although this fit is not shown to be statistically significant. This may indicate these procedural differences, or differences in the CIGS, to have a more profound effect on results than the thioacetamide/ InCl_3 exposure.

To better determine whether the thioacetamide treatment significantly affected the device performance as compared to the non-thioacetamide treated control samples, additional control samples were completed in separate

device finishing runs and a t-test was performed. The results of the t-test are summarized in Table 3. The means of all device parameters are very similar for both the treated and untreated cases indicating that no significant improvement in device performance can be achieved upon thioacetamide treatment.

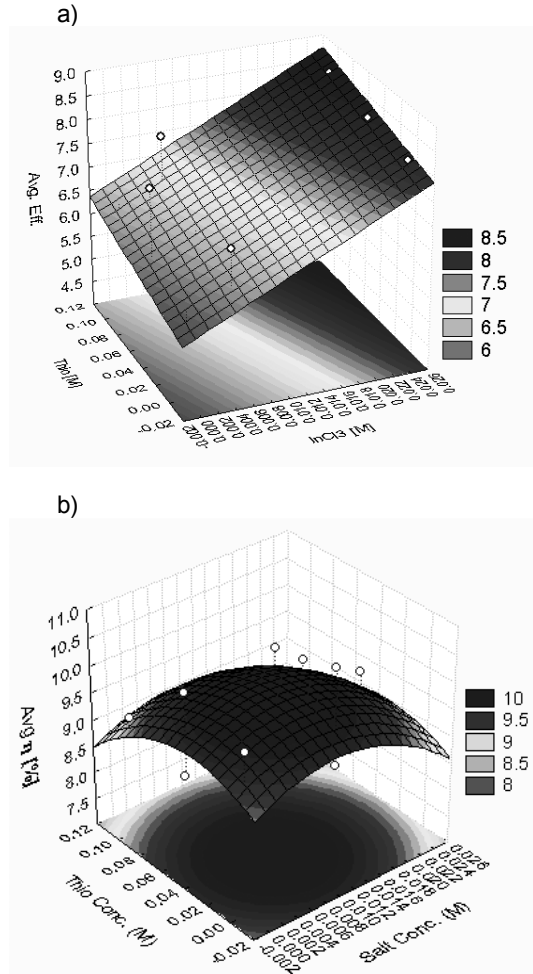


Figure 1. Statistical model fit to the average efficiency for the variables of salt and thioacetamide concentration for: (a) the single walled beaker set, and (b) the jacketed beaker set. Plots shown for the 6s immersion time only.

Figure 2 shows a box and whisker plot of the efficiency for thioacetamide treated samples (0) and untreated devices (1). Although not statistically significant, the mean efficiency of the untreated specimens is slightly higher than for the treated samples. Furthermore, a narrower distribution for the untreated samples is evident from the standard deviation (SD), indicating poor reproducibility of the thioacetamide process. Due to the larger number of treated devices the standard error (SE) is narrower as compared to

the untreated absorbers. Representative IV plots further illustrate that no significant difference can be observed between the two device groups (Figure 3).

Table 3. T-Test of thioacetamide treated samples and untreated controls. A p value of 0.95 indicates the probability that the two means are statistically identical at the 95% confidence level.

	Mean for Thio. Treated Samples	Mean for Control Samples	p
Avg η [%]	8.59	8.74	0.803
Avg V_{oc} [V]	0.583	0.588	0.741
Avg. J_{sc} [mA/cm^2]	23.64	23.03	0.255
Avg FF [%]	0.62	0.64	0.443

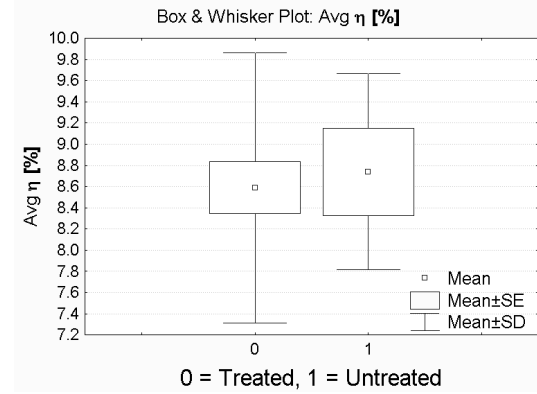


Figure 2. Box and whisker plot of efficiency for thioacetamide treated samples and control devices.

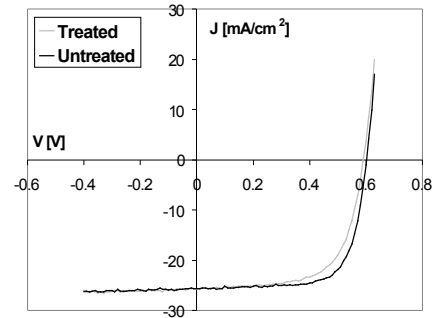


Figure 3. Representative current-voltage trace for a treated and an untreated device.

Bias-dependent QE measurements for devices based on treated and untreated absorbers show identical behavior (Figure 4). AES depth profiling on various as-deposited CIGS absorbers and subsequent device E_g

modeling – dividing the absorber into 8 E_g sections – yielded excellent agreement between experimental and theoretical QE plots for surface E_g values of 1.05 to 1.12 eV for the top 300 nm. Poor collection from the bulk, as evident from a current drop at higher wavelength, can be assigned to the high Ga content towards the back contact. With respect to the thioacetamide treatment, in contrast to Nakada et al. [1], the latter does not improve collection for the dual E_g -graded absorbers employed in this study.

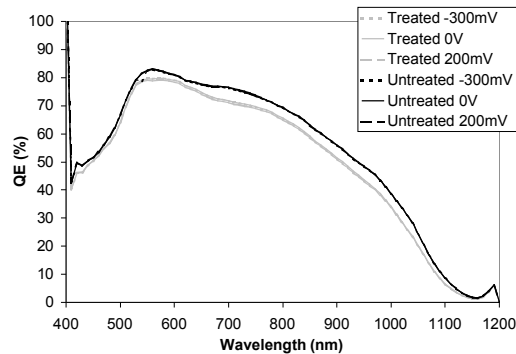


Figure 4. Bias-dependent quantum efficiency for treated and untreated devices.

Finally, identical zero voltage depletion widths of 0.24 μm and carrier concentrations of $3 \times 10^{16} \text{cm}^{-3}$ were measured via the capacitance-voltage technique.

Nakada, et.al. [1] suggested the addition of a wide bandgap material, such as In-S from thioacetamide/ InCl_3 treatment, at the junction to result in an increase in V_{oc} by reducing the conduction band offset between the CIGS and CdS. However, in the present study a thioacetamide treatment step did not yield improved V_{oc} values. Dullweber et al. [4] have shown that for dual E_g -graded absorbers – surface $E_g \approx 1.15 \text{eV}$ – the substantial gain in V_{oc} ($\approx 60 \text{ mV}$) over standard absorbers can be attributed to the high Ga content near the Mo back contact and a narrower low E_g region. As the V_{oc} values in the present study exceed those obtained in [4], it is likely that no additional benefit can be derived from the thioacetamide treatment for such Ga graded absorbers.

It was also suggested that formation of a thin wide bandgap sulfide layer at the CIGS surface results in a reduced surface recombination velocity of minority carriers, in turn raising J_{sc} [1]. Alternatively, passivation of defects at the surface of the CIGS via sulfur incorporation would increase J_{sc} [1]. No statistically significant increase in J_{sc} could be confirmed in the present study. The latter may be due to different CIGS surface properties or buffer/window variables.

CONCLUSIONS

No significant improvement in device performance due to thioacetamide treatment was detected. Absorber aspects not yet sufficiently investigated appear to have an important effect on resulting device performance. Minor convoluting impacts may also result from procedural details as evident from the differences observed for the two treatment formats. To date the thioacetamide treatment described in the literature was not found to be effective in increasing device performance on GSE CIGS.

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